



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/DK93/00167 <b>(22) International Filing Date:</b> 18 May 1993 (18.05.93)  <b>(30) Priority data:</b> 639/92                      18 May 1992 (18.05.92)                      DK  <b>(71) Applicant (for all designated States except US):</b> NOVO NORDISK A/S [DK/DK]; Novo Allé, DK-2880 Bagsvaerd (DK).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> YDE, Birgitte [DK/DK]; Tornehøj 148, DK-3520 Farum (DK).  <b>(74) Common Representative:</b> NOVO NORDISK A/S; Patent Department, Novo Allé, DK-2880 Bagsvaerd (DK).		<b>(81) Designated States:</b> AU, BR, CA, FI, JP, NO, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PRODUCTION OF A LIGNIN SOLUTION OR GEL, OF A BINDER AND OF A WOOD COMPOSITE  <b>(57) Abstract</b>  A solution or gel of lignin at high concentration free of solids is obtained by treating the lignin at high pH and then lowering pH to the desired value. Further, a binder for wood products (such as particle board) is produced by preparing a lignin solution or gel in this way and treating said solution or gel with a phenol oxidizing enzyme system (such as laccase or peroxidase).		

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## PRODUCTION OF A LIGNIN SOLUTION OR GEL, OF A BINDER AND OF A WOOD COMPOSITE.

### TECHNICAL FIELD

This invention relates to a method of preparing a solution or gel of lignin  
5 at high concentration, to a method of preparing a binder using said solution or gel,  
and to a method of producing a wood composite using said binder.

### BACKGROUND ART

It is known from US 4,432,921 to treatment of lignin with a phenol  
oxidizing enzyme to prepare a binder, and to use this binder for coating wood  
10 particles to produce a particle board. The enzymes are known to be active at weakly  
acidic to neutral pH.

For ease of applying the binder e.g. by spraying, it is desirable to  
provide the lignin as a solution or gel free of solids, and in order to obtain a strong  
particle board, it is desirable to use a high lignin concentration, but lignin is only  
15 sparingly soluble in water at weakly acidic to neutral pH.

### STATEMENT OF THE INVENTION

We have found that, surprisingly, a solution or gel of lignin free of solids  
can be obtained by treating the lignin at high pH and then lowering pH to the  
desired value.

20 Accordingly, the invention provides a method of preparing a solution or  
gel of lignin, characterized by comprising:

- a) treatment of the lignin above pH 8, followed by
- b) lowering the pH below 7.

Further, the invention also provides a method for producing an active binder for wood products from lignin, characterized by comprising preparation of a lignin solution or gel according to any preceding claim, and treating said solution or gel with a phenol oxidizing enzyme system. Finally, the invention provides a method of producing a wood composite from wood fibre material, characterized by comprising production of a binder according to claim 6, coating the wood fibre material with said binder, followed by pressing and heating.

## DETAILED DESCRIPTION OF THE INVENTION

### Lignin

10           The invention is applicable to any quality of lignin, particularly non-sulfonated lignin such as indulin which results in a strong binder when treated with a phenol-oxidizing system, but has a low solubility in water at weakly acidic to neutral pH where these enzymes are mostly active.

### Process conditions

15           Step b) is conveniently conducted by holding at pH 5-7 for 5-30 minutes at 10-50°C.

A lignin solution can be obtained by conducting step a) at pH 8-9.5 for 5-30 minutes at 20-100°C (preferably 60-100°C), and removing solids after step b), e.g. by filtration or centrifugation.

20           A lignin gel can be obtained by conducting step a) at pH 9.5-10.5 for 5-30 minutes at 20-100°C (preferably 60-100°C).

pH tends to drop during step a) and to rise during step b). The pH can be kept in the indicated ranges by continuous or repeated pH adjustment or by use of a buffer at a sufficiently high concentration (e.g. above 0.4 M).

25           Lignin can be used in an amount of 25-250 g/l, and solutions or gels containing above 100 g/l of lignin can be obtained.

### Phenol oxidizing enzyme system

The enzyme system used in the invention consists of a suitable oxidase together with  $O_2$  or a suitable peroxidase together with  $H_2O_2$ . Suitable enzymes are those which oxidize and polymerize aromatic compounds such as phenols and 5 lignin.

Examples of suitable enzymes are catechol oxidase (EC 1.10.3.1), laccase (EC 1.10.3.2) and peroxidase (EC 1.11.1.7). Some preferred enzymes are peroxidase derived from a strain of *Coprinus*, e.g. *C. cinereus* or *C. macrorhizus*, peroxidase from *Bacillus*, e.g. *B. pumilus* and laccase from *Trametes*, e.g. *T.* 10 *versicolor* (previously called *Polyporus*). It may be preferable to use two different phenol oxidizing enzymes together.

The amount of enzyme should generally be in the range 10-10,000 PODU or laccase units per g of lignin solid (activity units defined below).

Molecular oxygen from the atmosphere will usually be present in 15 sufficient quantity. A suitable amount of  $H_2O_2$  will usually be in the range 0.01-10 mM, particularly 1-10 mM.

### Production of binder

Suitable conditions for the enzymatic treatment of lignin to produce binder are known in the art. Typical conditions are 20-60°C and pH 5-6 for laccase, 20 and 20-60°C and pH 7-8 for peroxidase.

### Production of wood composite

Application of the binder to wood fibre material and pressing under heat to produce a wood composite can be done by methods known in the art. A typical example is production of particle board from wood particles. Typically, the binder is 25 applied by spraying in an amount of 40-100 g/kg of wood fibre material, and pressing is typically done by compressing for 2-4 minutes at a pressure of 20-40 kg/cm<sup>2</sup> (2-4 Pa) with temperature rising from 35 to 190°C in 20 seconds.

**EXAMPLES****Example 1**

125 mg/ml of indulin in buffer (Britton & Robinson) at pH 8, 9 or 10 was held for 15 minutes at 80°C with stirring. The pH value was kept constant by addition of 1 N NaOH.

Conditions were changed to pH 7 and room temperature, and the pH value was held constant by addition of 0.5 N acetic acid. Samples taken immediately after pH adjustment and after 10, 20 and 30 minutes were centrifuged for 5 minutes at 10,000 rpm, and the amount of lignin in solution was then determined by measuring OD 280 nm. Results:

pH in first step	Min. at pH 7	mg/ml lignin
8	0	77.2
	10	80.4
	20	68.65
	30	73.4
9	0	112.6
	10	98.4
	20	94.7
	30	81.0
10	0	85.1
	10	38.1
	20	44.0
	30	47.3

The samples pretreated at pH 8 and 9 were solutions from which undissolved lignin could be removed by centrifugation. The samples pretreated at pH 10 were gels, and the results shown above are for the remaining solution after removal of gelled lignin by centrifugation. These gels were suitable as such for production of binder, reacting more rapidly with peroxidase and giving a stronger binder than untreated lignin.

In a comparative experiment, 125 mg/ml of indulin in buffer at pH 7.0 was kept at 80°C (no further pH adjustment). After 15 minutes (pH 6.4), it was centrifuged, and the amount of lignin in solution was determined as above to be 18.5 mg/ml.

**CLAIMS**

1. A method of preparing a solution or gel of lignin, characterized by comprising:
  - a) treatment of the lignin above pH 8, followed by
  - 5 b) lowering the pH below 7.
2. A method according to Claim 1, wherein the lignin is non-sulfonated, preferably indulin.
3. A method according to either preceding claim, wherein the pH in step b) is maintained at 5-7 for 5-30 minutes at 10-50°C.
- 10 4. A method of preparing a lignin solution according to any preceding claim, wherein step a) is conducted at pH 8-9.5 for 5-30 minutes at 60-100°C, and wherein solids are removed after step b).
5. A method of preparing a lignin gel according to any of Claims 1 - 3, wherein step a) is conducted at pH 9.5-10.5 for 5-30 minutes at 10-50°C.
- 15 6. A method for producing an active binder for wood products from lignin, characterized by comprising preparation of a lignin solution or gel according to any preceding claim, and treating said solution or gel with a phenol oxidizing enzyme system.
7. A method of producing a wood composite from wood fibre material,  
20 characterized by comprising production of a binder according to Claim 6, coating the wood fibre material with said binder, followed by pressing and heating.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 93/00167

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08L 97/00, C09J 197/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C08L, C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4432921 (ANNEGRET HAARS ET AL), 21 February 1984 (21.02.84) --	1-7
A	US, A, 4357454 (KRISTER HOLMBERG ET AL), 2 November 1982 (02.11.82) --	1-7
A	DE, C1, 3644397 (G.A. PFLEIDERER UNTERNEHMENSVERWALTUNG GMBH & CO KG), 5 May 1988 (05.05.88) -----	1-7

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

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Parent document cited in search report		Publication date	Patent family member(s)		Publication date
US-A-	4432921	21/02/84	DE-A,C-	3037992	19/08/82
US-A-	4357454	02/11/82	JP-A-	57076056	12/05/82
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			SE-T3-	0275544	